Assessment of density functional approximations: long-range correlations and self-interaction effects

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The complex nature of electron-electron correlations is made manifest in the very simple but non-trivial problem of two electrons confined within a sphere. The description of highly non-local correlation and self-interaction effects by widely used local and semi-local exchange-correlation energy density functionals is shown to be unsatisfactory in most cases. Even the best such functionals exhibit significant errors in the Kohn-Sham potentials and density profiles.

I. INTRODUCTION

The Kohn-Sham (KS) [1] formulation of Density Functional Theory (DFT) [2] is in the present day the most popular method in electronic structure calculations. In this scheme, the exact ground state energy and electron density could be found self-consistently if the exchange-correlation (XC) energy functional $E_{\rm XC}[n]$ was known. $E_{\rm XC}[n]$ contains all the quantum many-body effects of the electron system, but very simple mean-field prescriptions like the Local Density Approximation (LDA) often suffice to obtain accurate results for a wide variety of systems at an affordable computational cost.

However, there are several problems that are well beyond the capabilities of the local approximation and any *semi-local* extension thereof, because of the clear manifestation of the very non-local nature of electron-electron correlations. For example, the long-ranged van der Waals interactions, the image potential at metal surfaces and clusters, or several *pathological* behaviors of the exact XC potential cannot be described at all using simple XC functional models [3]. Nevertheless, these limitations should not be important in many other situations, and new XC functionals are being proposed with the aim of reaching chemical accuracy while keeping the implementation ease of the local density based approximations [4, 5]. This could open the appealing possibility of making predictive studies of relevant aspects of Quantum Chemistry such as reaction paths, atomization energies, and bond lengths and energies.

The purpose of this paper is to bring further insight in the capabilities and limitations of local and semi-local XC functionals, showing that even in very simple problems the complexity of the quantum electron-electron correlations might prevent any of these approaches from properly describing the ground state properties of such systems. We do not intend to make a comprehensive assessment of mean-field-like approximations, but just to provide a representative common picture of all them. Hence, among the realm of proposals existing in the liter-

ature, we have chosen the well-known LDA prescription by Perdew and Wang [6], the Generalized Gradient Approximation (GGA) by Perdew-Burke-Erzenhof [7], and the very recent meta-GGA (MGGA) proposed by Tao *et al* [8]. These three approaches have the virtue of being designed using general considerations (i.e. they do not include empirical parameters). Furthermore, they can be seen as a coherent set of conceptual progressive improvements starting from the strictly local approximation, then considering the dependence on the density variation, and finally including information from KS orbitals through its associated kinetic energy density.

We will study a very simple but non-trivial system: two electrons confined within a sphere of hard walls, whose solution has been found through accurate Configuration Interaction calculations [9, 10]. This system is an interesting benchmark reference due to the following reasons. First, its simplicity: the density is isotropic, hence having a simple mathematical one-dimensional problem restricted to the radial coordinate. Second, its ground state has singlet spin configuration. As a consequence, Pauli's correlation (exchange) between the electrons is absent and the exchange energy $E_{\rm X}[n]$ just corrects the spurious electron self-interaction in the classical Hartree electrostatic energy $W_{\rm H}[n]$. That is, the Coulomb correlation is actually the only source of quantum many-body effects in this system. Finally, different correlation regimes can be easily achieved by varying the radius R of the confining sphere. Thus, at small R (high mean density) we are in the low-correlation limit where the confinement by the sphere dominates over the electron-electron interaction, so having a system with an *atomic-like* behavior. By increasing the value of R (decreasing the mean density) we gradually enter into a highly correlated regime in which the correlation exhibits long-ranged and anisotropic effects.

Then, this simple system offers an excellent scenario to assess essential features of functional approximations to the XC energy. In particular, since it is impossible within the present formulation of semi-local functionals

TABLE I: Comparison between the exact exchange and correlation energies for several sphere radii R and the results given by the local and semi-local functionals evaluated on the exact density profile. The exact total energy is also included to illustrate the increasing importance of correlation for high R.

R	$E_{\rm tot}^{\rm ex}$	$E_{\rm X}^{\rm ex}$	$E_{\rm X}^{\rm LDA}$	$E_{\rm X}^{\rm GGA}$	$E_{\rm X}^{\rm MGGA}$	$E_{\rm C}^{\rm ex}$	$E_{\rm C}^{\rm LDA}$	$E_{\rm C}^{\rm GGA}$	$E_{\rm C}^{\rm MGGA}$
1	11.5910	-1.7581	-1.5230	-1.6843	-1.7805	-0.0507	-0.1424	-0.0775	-0.0647
5	0.7016	-0.3335	-0.2914	-0.3213	-0.3412	-0.0383	-0.0715	-0.0501	-0.0421
10	0.2381	-0.1592	-0.1407	-0.1550	-0.1651	-0.0288	-0.0481	-0.0362	-0.0301
25	0.0633	-0.0590	-0.0537	-0.0596	-0.0634	-0.0163	-0.0257	-0.0201	-0.0166
50	0.0249	-0.0278	-0.0262	-0.0296	-0.0311	-0.0093	-0.0151	-0.0116	-0.0095

to achieve the exact exchange energy for arbitrary one- and two- electron systems ($-W_{\rm H}[n]$ and $-W_{\rm H}[n]/2$ respectively), we can easily see how important is this limitation for two-electron densities with very distinct mean densities. On the other hand, LDA and GGA suffer from spurious correlation self-interaction, a limitation which is corrected by the MGGA [8, 11]. Nonetheless, the proper self-interaction correction does not guarantee the overall accuracy of the correlation functional, and the actual role played by non-local correlation effects has to be checked carefully.

As a first test, we will evaluate these functionals over the exact densities, i.e. in a non-self-consistent fashion, comparing the XC energies and potentials with the exact ones. Then, we will present the fully self-consistent solutions, in such a way that we will assess not only the self-consistent energies but also the DFT densities that minimizes the corresponding total energy functionals. Atomic units ($\hbar = m_e = e = 1$) will be used throughout the paper.

II. RESULTS ON THE EXACT DENSITY PROFILE

The Hamiltonian of the two-electron model system is given by

$$\hat{H} = -\frac{1}{2}\sum_{i=1}^{2}\nabla_i^2 + \frac{1}{|\vec{r}_1 - \vec{r}_2|} + \sum_{i=1}^{2}V(r_i)$$

$$V(r) = \begin{cases} 0 & r < R \\ \infty & r \geq R. \end{cases}$$

The hard wall described by $V(r)$ impose strict boundary conditions at $r = R$, but does not have a direct contribution to the total energy functional $E[n]$. Therefore:

$$E[n] = T_{\rm S}[n] + W_{\rm H}[n] + E_{\rm XC}[n] , \qquad (1)$$

where $T_{\rm S}[n]$ is the kinetic energy of the fictitious KS non-interacting system. For a singlet state, the set of KS equations is reduced to a single Schrödinger equation

$$\left[-\frac{1}{2}\nabla^2 + v_{\rm S}(\mathbf{r})\right]\phi(\mathbf{r}) = \varepsilon\phi(\mathbf{r}) , \qquad (2)$$

where $v_{\rm S} = v_{\rm H} + v_{\rm X} + v_{\rm C}$ is the KS effective potential which is the sum of the Hartree ($v_{\rm H}$), exchange ($v_{\rm X}$), and correlation ($v_{\rm C}$) potentials. The density is related to the ground-state orbital of (2) through the simple equality $\phi(\mathbf{r}) = \sqrt{n(\mathbf{r})/2}$.

Under the exact DFT formulation, if $n^{\rm ex}(r)$ is the ground-state density of the system, the corresponding eigenvalue $\varepsilon^{\rm ex}$ must equal the ionization energy $E[n^{\rm ex}] - E^{(1)}$, where $E[n^{\rm ex}] = E_{\rm tot}^{\rm ex}$ is the two-electron ground state energy and $E^{(1)} = \pi^2/(2R^2)$ is the energy of the one-electron system. Thus, the exact correlation potential can be written explicitly as

$$v_{\rm C}^{\rm ex}(\mathbf{r}) = \varepsilon^{\rm ex} + \frac{1}{2}\frac{\nabla^2\sqrt{n^{\rm ex}(\mathbf{r})}}{\sqrt{n^{\rm ex}(\mathbf{r})}} - \frac{1}{2}\int d\mathbf{r}'\frac{n^{\rm ex}(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|}, \qquad (3)$$

where we have used the exact relation $E_{\rm X}[n] = -W_{\rm H}[n]/2$.[13] However, it is worth pointing out that (3) is an expression only valid for the exact density profile. An exact functional expression for the correlation potential $v_{\rm C}(\mathbf{r})$ of an arbitrary spin-unpolarized two-electron density $n(\mathbf{r})$ would require to know the external potential that defines the two interacting electron system whose ground state is $n(\mathbf{r})$ and then include such a potential. Then, the simplicity suggested by (3) is just apparent.

The performance of different local and semi-local prescriptions when evaluating the XC energy on the exact density profile is shown in Fig. 1 and Table I. The LDA systematically underestimates the absolute value of the exchange energy, whereas the GGA partially corrects this trend, although in the low density limit the GGA overestimates $|E_{\rm X}|$. The MGGA behaves reasonably well for small radii, which is not a surprise since it reproduces exactly the exchange energy of the hydrogen atom and, as we said in the Introduction, in this range the model system behaves precisely like an atom. Thus, although the MGGA does not cancel exactly the spurious Hartree self-interactions, it fairly accounts for such a cancellation in atomic-like systems. When decreasing the mean electron density, the system cannot be considered like an atom any more and the MGGA greatly overestimates the self-interaction corrections to $W_{\rm H}$, becoming even worse than GGA.

Regarding the correlation energy $E_{\rm C}[n]$, the LDA shows an evident poor behavior which is improved by the GGA although the correlation energies are always much
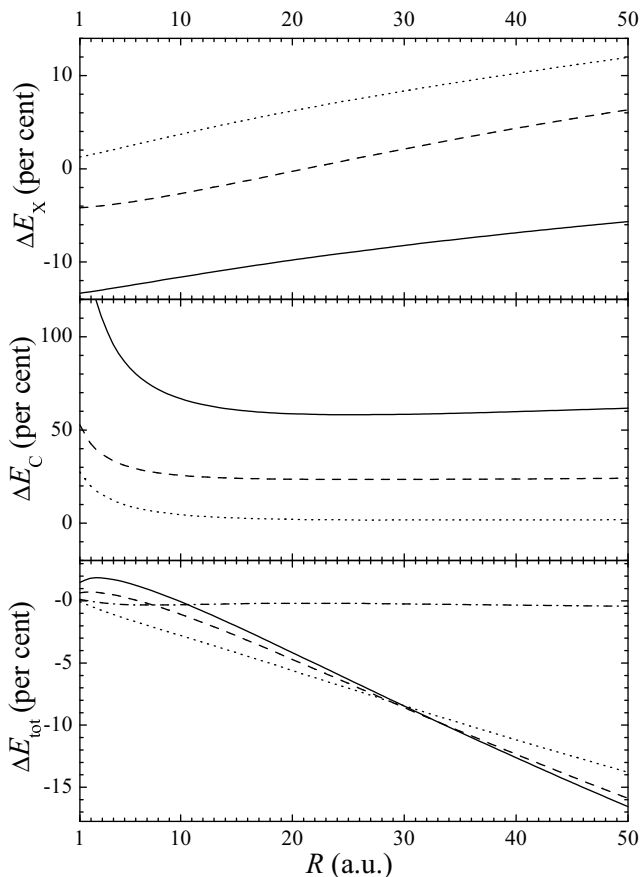
FIG. 1: Percent errors $\Delta E = 100 \times \left(E^{\mathrm{DFT}} - E^{\mathrm{ex}}\right)/E^{\mathrm{ex}}$ for the exchange, correlation, and total energies as functions of the sphere radius R. All DFT results are obtained non-self-consistently over the exact density. Solid line: LDA; dashed line: GGA; dotted line: MGGA; dash-dotted line: EXX+M.

FIG. 2: Exchange and correlation potentials obtained from the exact density profile ($R = 10$). Thick solid line: exact results; thin solid line: LDA; dashed line: GGA; dotted line: MGGA; dash-dotted line: EXX+M. Note that the shape of the LDA XC potential reproduces fairly well the exact one excepting in the region around the center of the sphere. This error is amplified by the EXX+M prescription, where the exchange part is exactly correct but the correlation potential is the same as the MGGA.

too negative. On the contrary, the MGGA behaves extremely well for all densities. Its relative error in the high density limit (around 20%) has a minor influence in the total energy, and such an error is less than 5% for lower densities. This excellent performance is in agreement with the conclusions by Seidl *et al* [12] about the essentially correct behavior of the meta-GGA correlation functional proposed in Ref. 11 (the basic ingredient of the MGGA by Tao *et al*) under uniform scaling to the low density limit. We have to bear in mind that in the highly correlated regime, the two electrons are *localized* in two different positions. That is, if one of the electrons is at a distance r from the center, the probability to find the second one is concentrated around a point on the opposite side [9]. Thus, the LDA/GGA main source of error in this regime, corrected by the MGGA, is the absence of self-interaction corrections.

In the lower panel of Fig. 1 we present the accuracy of the corresponding non-self-consistent DFT total energies. The well known compensation of errors between exchange and correlation in LDA and GGA is easy to observe in the atomic-like limit, but in the high corre-
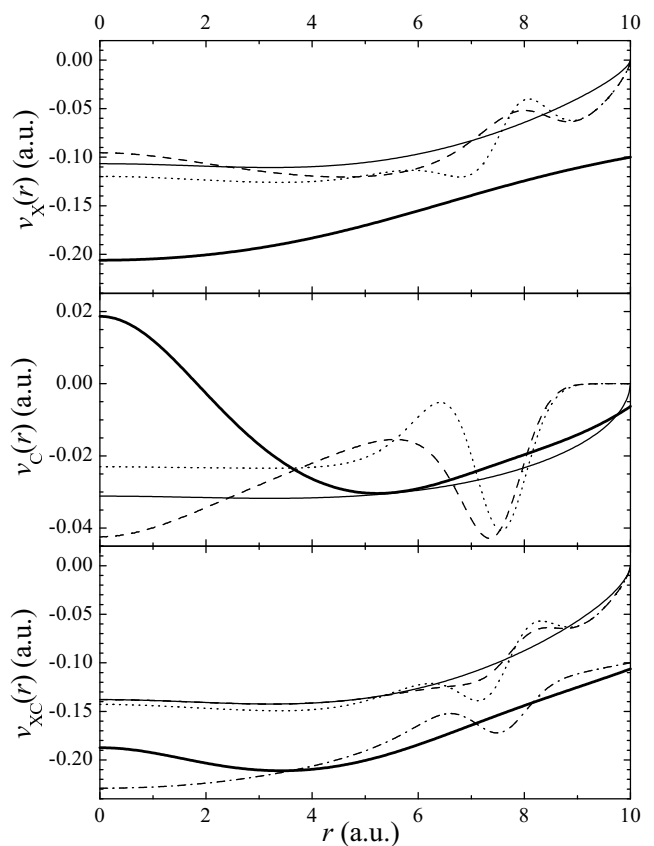
lation regime both functionals fail badly. The MGGA does not benefit from any cancellation of errors (it overestimates the absolute value of exchange *and* correlation energies). Hence, it slightly underestimates the total energy for small radii, but the error on exchange dominates for lower densities where the MGGA perfoms poorly. A hyper-GGA [5], designed with the aim of being free of any self-interaction error, must yield very accurate total energies for all the ranges in our model system. Then, its performance should be similar to the presented in the lower panel of Fig. 1, where we plot the relative error on the total energy evaluated through a hybrid functional, EXX+M, where the exchange is calculated exactly and the correlation approximated by the MGGA. In this case, the error on the total energy is always less than 1 %, and for $R \simeq 1$ the absolute deviation is just 7 mHa/e, fairly close to the chemical accuracy (around 2 mHa/e).

From the shape of the potentials it is possible to see the underlying physics contained in the approximations. The above mentioned *localization* of the electrons in the

highly correlated limit is an obvious consequence of the electrostatic repulsion, which tend to dominate over the confinement by the wall as we increase the radius of the system. Since the Hartree energy contains spurious self-interactions, the role of the exchange is to compensate partially the effects due to W_H. As we can see in the upper panel of Fig. 2, where $v_X(r)$ is plotted for the model system with $R = 10$, the exact exchange potential has a mininum in the center of the sphere, favouring an atomic-like behavior. The corresponding LDA potential is not able to account completely for this exchange *attractive* feature, whereas the overall shift of v_X^{LDA} is a concomitant consequence of the local dependence on the density. The semi-local potentials exhibit a similar behavior but there are unphysical oscillations reflecting the presence of the gradient and the Laplacian of the density in the expression of the exchange potential.

On the contrary, the Coulomb correlation enhances the localization through a potential barrier located in the center of the sphere (see the middle panel of Fig. 2). This barrier reflects a truly non-local correlation effect. In fact, for $R = 10$, the electron density is almost homogeneous around $r = 0$, and then $v_C^{LDA}(\mathbf{r})$ is practically constant in this region. On the other hand, the LDA fits reasonably well the exact potential if $r \gtrsim 5$, but this partial agreement is completely lost under the GGA and MGGA. This overall bad quality of the local and semi-local correlation potentials is a general feature in finite systems [14], although in some cases it could be masked if we focus on the total $v_{XC}(\mathbf{r})$. As we may see in the lower panel of Fig. 2, the XC potentials given by LDA, GGA, and MGGA are rather similar (excepting the above mentioned unphysical oscillations). Their shape is close to the exact one for $r \gtrsim 5$ but, as expected, they do not reproduce at all the correlation barrier at $r = 0$. Under the EXX+M prescription, the situation is even worse, since the XC potential reaches a minimum at $r = 0$ due to an exact description of exchange which is not compensated by an accurate correlation potential. Therefore, although the correlation energies given by the MGGA are excellent, the potentials derived from it are not able to reproduce the non-local effects that manifest themselves in the shape of $v_C(\mathbf{r})$. As we will see in the next section, this will lead to important deviations from the exact density profile when solving self-consistently the KS equation.

III. SELF CONSISTENT RESULTS

One of the major advantages of KS-DFT is its fully self-consistent character: any previous knowledge of the electron density profile is not required excepting for setting up an initial guess to start the iterative resolution of the KS equations. For many purposes, LDA and/or GGA give accurate self-consistent densities because the corresponding approximate potentials are very similar to the exact ones in those regions relevant for the calculation of the electron density. This justifies the use of more sophis-
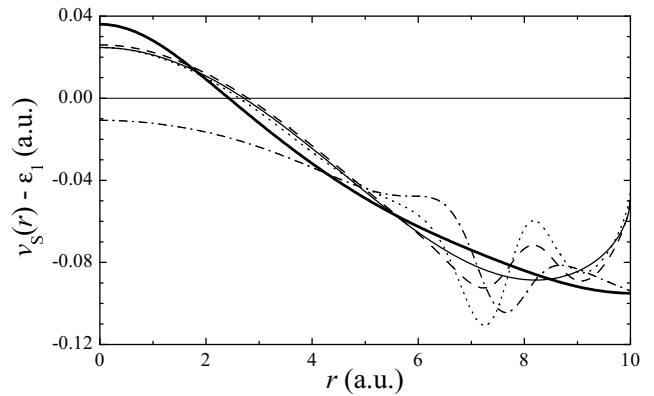

FIG. 3: Kohn-Sham potential $v_S(r)$ for the exact density profile ($R = 10$). Thick solid line: exact result; thin solid line: LDA; dashed line: GGA; dotted line: MGGA; dash-dotted line: EXX+M. In order to allow an easier comparison, the potentials have been shifted in such a way that the corresponding first eigenvalue for each approximate potential is equal to zero. The behavior of the potentials near the sphere walls is less important due to the role played by the boundary condition $n(R) = 0$.

ticated functional expressions as a mere correction over the self-consistent LDA/GGA densities. Consequently, the main effort carried out during the last years had been directed towards the improvement of the XC energies, paying less attention to the characteristics of the XC potential $v_{XC}(\mathbf{r})$.

Nonetheless, in the previous section we have seen that all the functionals considered in this paper fail to reproduce the exact XC potential in a region where the electron density is far from being negligible. The consequences can be seen in Fig. 3, where we compare the exact KS potential $v_S(r)$ with the DFT ones obtained from the exact density profile $n^{ex}(r)$. The LDA, GGA, and MGGA do not reproduce the exact shape of $v_S(r)$ and it is reflected by a classical forbidden region greater than the actual one: the self-consistent density will be pushed towards the walls. The EXX+M model, as comented, incorporates exactly the attractive character of exchange, but the wrong description of $v_C(r)$ makes the effective potential less confining than the exact one: this hybrid approach tends to concentrate the density around $r = 0$.

These deviations from the exact two-electron density profile, which can be quantified through the expression

$$\delta n = \frac{1}{2} \int d\mathbf{r} \, |n^{ex}(\mathbf{r}) - n(\mathbf{r})| \, , \qquad (4)$$

should not be important for high mean densities. In this atomic-like limit the external confining potential dominates, and the electrons are going to be concentrated around the center of the sphere anyway. However, the greater the radius the less important the confinement, and the shape of the XC potential will play a more prominent role. This trend can be seen in Fig. 4, where we
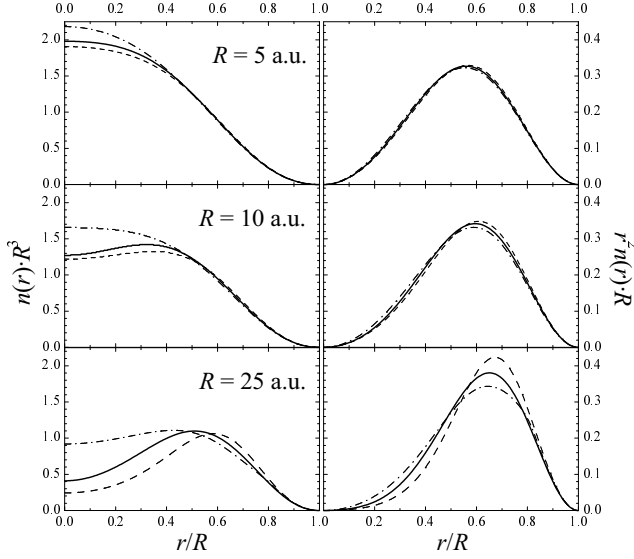
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FIG. 4: Exact (solid line) and self-consistent GGA (dashes) and EXX+M (dash-dots) densities $n(r)$ and reduced radial densities $r^2 n(r)$. All the quantities have been scaled with the radius of the confining sphere. The self-consistent LDA and MGGA densities are very similar to the GGA ones and have not been included in the figure. None of the approximate functionals is able to reproduce the correct behavior of the density in the center of the sphere, and their overall performance is very poor for $R \gg 0$.

TABLE II: Self-consistent DFT-KS results for several radii compared with the exact ones. The last file of each entry contains the DFT density error δn as defined in Eq. 4.

	Exact	LDA	GGA	MGGA	EXX+M
$R=1$					
E_{tot}	11.5910	11.7338	11.6376	11.5540	11.5770
$T_{\text{S}}+W_{\text{H}}$	13.3999	13.3955	13.3974	13.3973	13.4000
E_{X}	-1.7581	-1.5193	-1.6820	-1.7785	-1.7582
E_{C}	-0.0507	-0.1423	-0.0778	-0.0648	-0.0647
δn		0.0070	0.0049	0.0056	0.0006
$R=5$					
E_{tot}	0.7016	0.7104	0.7017	0.6897	0.6975
$T_{\text{S}}+W_{\text{H}}$	1.0734	1.0713	1.0716	1.0720	1.0747
E_{X}	-0.3335	-0.2897	-0.3196	-0.3401	-0.3348
E_{C}	-0.0383	-0.0713	-0.0504	-0.0421	-0.0423
δn		0.0210	0.0222	0.0196	0.0157
$R=10$					
E_{tot}	0.2381	0.2371	0.2346	0.2305	0.2362
$T_{\text{S}}+W_{\text{H}}$	0.4261	0.4245	0.4246	0.4249	0.4275
E_{X}	-0.1592	-0.1395	-0.1537	-0.1643	-0.1608
E_{C}	-0.0288	-0.0479	-0.0363	-0.0301	-0.0306
δn		0.0383	0.0448	0.0371	0.0401
$R=25$					
E_{tot}	0.0633	0.0587	0.0584	0.0582	0.0626
$T_{\text{S}}+W_{\text{H}}$	0.1387	0.1377	0.1376	0.1377	0.1395
E_{X}	-0.0590	-0.0533	-0.0597	-0.0632	-0.0600
E_{C}	-0.0163	-0.0256	-0.0195	-0.0163	-0.0170
δn		0.1352	0.1424	0.1300	0.0858
$R=50$					
E_{tot}	0.0249	0.0197	0.0199	0.0204	0.0243
$T_{\text{S}}+W_{\text{H}}$	0.0620	0.0621	0.0622	0.0623	0.0624
E_{X}	-0.0278	-0.0270	-0.0318	-0.0330	-0.0282
E_{C}	-0.0093	-0.0154	-0.0105	-0.0088	-0.0099
δn		0.3317	0.3348	0.3343	0.1084

compare the DFT densities $n(r)$ as well as the the corresponding reduced radial densities $r^2 n(r)$ with their exact counterparts. In the atomic-like regime ($R \lesssim 5$), we can observe genuine errors on the DFT densities around the center of the sphere. However, this wrong behavior will lead to marginal errors on integrated quantities, as suggested by the overall good agreement shown by the reduced radial densities. At intermediate mean densities ($R \simeq 10$), the differences on $r^2 n(r)$ can be already observed at a first glance. Moreover whereas the system shows an incipent localized behavior, which is characterized by a density reaching a local maximum at $r \neq 0$, the EXX+M self-consistent density still has an atomic behavior characterized by a maximum at $r = 0$. Finally, in the low density limit, all the approximate functionals fail to describe the exact density profile with a minimum accuracy. For instance, if $R = 25$ the error given by (4) is 8.6 % using the EXX+M functional and 14.2 % using the GGA.

Then, the full minimizimation of $E[n]$ adds a further source of error due to the inaccuracies of the self-consistent density. Nonetheless, these *self-consistency-induced* errors in the total energies are going to be less important because there is an overall trend to cancellation, see Table II. For instance, the EXX+M self-consistent density is smoother than the exact one, which lowers the kinetic and exchange energies while increasing the Hartree interaction energy. However, in spite of the distorted density profile, there is a fortunate cancellation of

errors that makes the sum of these three terms practically equal to the exact value. Thus, the minimization of the energy leads to changes on the density profile favoring lower correlation energies, which is done by increasing the density around the center of the sphere. As a result, self-consistent total energies are just slighty worse than the non-self-consistent ones, the relative error ΔE_{tot} ranging from -0.1% for $R = 1$ to -2.5% for $R = 50$. A similar conclusion reads for the remaining functionals (LDA, GGA, MGGA), although in this case the self-consistent $T_{\text{S}}[n]$ is greater than the exact one, whereas the classical interaction energy is reduced after the minimization. Hence, self-consistency keeps the fairly good quality of the total energies in the atomic limit, where there are minor changes in the density profile, and for intermediate and low densities the dramatic changes on $n(\mathbf{r})$ induce a few percent variation on the total energies that, in any case, were already too small.

IV. CONCLUSIONS

In this work we have assessed the quality of some of the most popular XC functionals used in *ab-initio* electronic structure calculations in a simple system of electrons where several correlation regimes can be easily achieved. None of the exchange functionals is completely free of self-interaction errors, making imposible to obtain accurate energies for highly correlated electrons. Local and GGA correlation exhibit a similar drawback, but the MGGA correlation shows an excellent performance for all the regimes. Nonetheless, neither LDA/GGA nor MGGA can describe highly non-local correlation effects that lead to a non-trivial behavior of the correlation potential, so seriously affecting the quality of the self-consistent densities. Due to persistent cancellation of trends, the corresponding changes on the total energy after minimization are less important, but this uncontrolled source of error might prevent these approximate functionals from having full predictive accuracy.

The overall bad quality of the self-consistent KS potential also compromises the evaluation of post-self-consistency corrections based on more sophisticated methods, like Many-Body Perturbation Theory or time-dependent DFT [3], if the wrong effective potential is not corrected as well. On the other hand, an accurate description of the XC potential is required, for instance, when studying neutral excitations in finite systems using time-dependent DFT [15]. As shown recently by Della Sala and Görling [16], for those systems having an HOMO orbital with nodal surfaces, the exact exchange potential tends to a constant if going to infinity over a set of zero measure directions. This leads to the appearance of potential barriers that, although could be of minor importance when obtaining the self-consistent static results, might be essential if a proper description of all the unoccupied KS orbitals was required. Here, although in a very different context, potential barriers induced by the non-locality of the many-body effects in an electron system have been observed as well.

The limitations observed for this family of prototype systems might have relevance for real molecular or condensed-matter systems in some cases. Prospective tests of the MGGA functional used in this work show an excellent performance for a wide variety of typical molecular and solid state systems which, moreover, seems to be kept if partial self-consistency is achieved [8]. However, there is no guarantee that the energy minimization procedure may lead to small, but relevant changes on the local electron density in, for instance, the bonding region between two species, so giving a wrong account of the nature of such a chemical bond. Finally, for this model system we have seen that there are not substantial differences between the fully self-consistent GGA and MGGA densities, although in this case the MGGA functionals take a simple GGA-like form. In spite of this simplification, the MGGA-XC potential amplifies the spurious oscillations already appearing under the GGA prescription. As a conclusion, the overall capability of MGGA and envisaged improvements thereof to yield accurate XC energies can hardly be questioned (specially for the correlation part), but further studies of the actual performance of the corresponding KS potentials are required. The latter point is relevant for those situations in which LDA/GGA are not able to reproduce the electron density with the requiered accuracy, and for other DFT-based applications needing an overall good description of $v_{\rm S}(\mathbf{r})$.

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